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(12) UK Patent Application (19) GB (11) 2 233 334 (13) A

(43) Date of A publication 09.01.1991

(21) Application No 8915000.7

(22) Date of filing 29.06.1989

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(51) INT CL[5]
C08J 3/28 7/18

(52) UK CL (Edition K)
C3L LJE LJX L130
C3W W100 W223 W314 W317
U1S S1345 S1363 S1582 S1632 S2068 S3031 S3038 S3077

(56) Documents cited
EP 0233755 A

(58) Field of search
UK CL (Edition K) C3L LJD LJE LJX
INT CL[5] C08F, C08J
Online databases: WPI

(54) **Surface treatment of polymer materials by the action of pulses of UV radiation**

(57) The uses and applications of polymer films and other materials that have had their surfaces modified chemically or structurally by the action of one or more pulses of high power ultra violet radiation from both incoherent and coherent pulsed excimer lasers are disclosed. The applications of such surface treatment include surface cleaning, generation of free electrical charges, adhesive bonding, increasing friction, reducing light reflection, making micro particle filters, marking, making field emission cathodes, catalyst substrates, and making hydrophobic surfaces hydrophilic.

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The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1982.

APPLICATIONS AND USES OF POLYMER MATERIALS WITH SURFACE REGIONS ACTIVATED AND MICROSTRUCTURED BY THE ACTION OF PULSES OF UV LASER RADIATION

The inventions described here relate to the uses and applications of polymer films and objects that have had surface areas modified chemically or structurally by the action of one or more successive pulses of ultraviolet radiation from pulsed excimer lasers.

It is well known that when the short duration, high intensity pulses of radiation from ultraviolet excimer lasers operating in the wavelength region between 190 and 351nm are directed onto the surface of polymeric materials, a thin layer of the irradiated region in which the incident radiation is strongly absorbed is decomposed and dissociated by bond scisson into low molecular weight fragments which ablate from the surface at high velocity.

This process is termed ultraviolet photoablation or photochemical etching and because of the very low level of thermal damage caused to the material or surrounding polymer it has been used widely to create microstructures such as hole arrays or channels in a variety of polymers. The depth of material removed by each pulse of laser radiation is a function of the polymer, the laser wavelength and fluence (Joules per cm^2) but is usually in the range of a fraction to several micrometers. Consequently structures with depths up to fractions of or over many millimeters can be cut with high precision into polymers by the action of hundreds to thousands of consecutive pulses on the same area.

This patent is concerned not with the cutting of such deep well defined structures in polymers but with the excimer laser induced chemical and structural modification of the top layer of the flat and generally smooth surface of various polymers to produce either microscale surface irregularities or chemically clean and activated regions or areas with free surface charges. With such excimer laser treatment the surface behaviour of the polymer material is modified and enables it to be used for a wide variety of applications in medical, chemical, biomedical, electrochemical and related areas.

Several excimer laser based *methods* exist for converting the generally smooth, relatively inert and possibly contaminated surface of polymer films and sheets into more chemically clean and active ones which contain free surface charges or into surfaces with micro-irregularities.

1) In one method one or more pulses of excimer laser radiation with a fluence in the range a fraction to several joules per square cm are allowed to interact with the

surface of most polymer films. With correct choice of material, laser wavelength and laser fluence various types of interaction occur. Whatever the material the laser wavelength and fluence can be chosen such that the first laser pulse interacts strongly with any hydrocarbon contamination layer on the surface causing it to ablate and to leave behind a clean and active surface. In some cases more than one laser pulse may be necessary to remove all contamination.

If the base polymer material has a low absorption under the conditions used and the fluence does not exceed the threshold for ablation then after the surface layer is removed no further ablation occurs. If the polymer material has high absorption at the conditions used such that the threshold for ablation is exceeded, then the effect of succeeding pulses will be to remove thin layers of polymer and to give rise after a few pulses to a highly active polymer surface with a high density of free surface charges. Such a surface is produced by the action of excimer laser radiation of short enough wavelength on almost any polymer. Depending upon the polymer material used, the etched surface may be smooth or rough.

2) In a second method, one or more pulses of excimer laser radiation with fluence in the range of a fraction to several joules per cm^2, are allowed to interact with the surface of semicrystalline polymers such as polyethylene terphathalate (PET), polyvinylidene fluoride (PVDF), polyetheretherketone (PEEK) or with polymer films that have been stretched, oriented or aligned during manufacture such as Makrofol (a trademark of Bayer Corp polycarbonate material). Such semicrystalline materials contain microcrystallites of a few micrometer size that are of higher density and have different uv light absorptive properties compared to the amorphous regions between them. Consequently the depth of material ablated by each excimer laser pulse is different for the two different components of the film. In general the higher density crystalline regions etch at a slower rate than the amorphous regions. Thus after one or more laser pulses have irradiated the surface it becomes rough and irregular having peak to peak scale length of the order of a few to a few tens of micrometers and is of the general scale size of the microcrystallites. Depending upon the material, the laser wavelength, the laser fluence and the number of laser pulses, a variety of structure scale sizes and heights ranging from submicrometer to several micrometers can be produced. Deeper structures will be produced as the number of laser pulses is increased.

In a similar way polymer films that have been stretched or oriented during manufacture have regions where the polymer bonds have been disrupted which lead to variations in the laser etching rate . Such smooth surfaced films when subjected to one or more pulses of excimer laser radiation, are converted into roughened regions with a wide variety of scale size ranging from sub to many micrometers. These structures are often in the form of channels or troughs aligned with or

perpendicular to the direction of the stretching of the film. Using the methods described above the surface irregularities can be enhanced by careful choice of laser wavelength and fluence.
With appropriate conditions polymer material can be made to jet up from the surface during laser irradiation and cool and solidify after the pulse. Such surfaces contain upstanding columns of polymer which resist further etching due to their steep angle to the incoming laser beam. After several laser pulses such surfaces take on the appearance of fibrous matted material.

3) In a third method very fine submicrometer scale structures can be produced on the surface of polymers with a single pulse from an excimer laser. In this case the laser must be arranged to emit pulses that are both temporally and spatially coherent such that when two parts of the beam are split apart and overlapped at an angle on the surface of the film interference fringes are produced which cause modulation of the beam intensity. Upon irradiation of the polymer this modulation causes a fine linear grating structure to be etched onto the surface.
The laser fluence required for this treatment depends upon the type of polymer and laser wavelength but is generally in the range of a fraction to a few J/cm^2. The grating depth etched by a single laser pulse is generally a fraction of a micrometer. Line spacing is controlled by the angle of combination of the two beams at the polymer surface and can be made as small as 0.2-0.3 micrometers. A suitable convenient method for splitting the excimer laser beam into two parts and combining at the surface of the film to produce a linear grating structure on a single laser shot using a biprism has been described [1].
The structure produced by this method gives rise to a linear grating structure with all lines running in one direction. A much more irregular pattern can be made by producing two or more such linear grating structures at differing angles using either a single biprism with multiple laser pulses and rotating the film between successive pulses or by using a single pulse exposure with optical components such as prisms or splitters to divide the beam into four or more parts which are then combined at different angles at the film surface . Double biprism devices have been described as a method to produce homogeneous beam profiles from temporally and spatially incoherent excimer lasers [2] and are ideal devices for producing two orthogonally aligned gratings when used to recombine the output produced by a much more coherent excimer laser. The etched structure has the appearance of a regular array of submicrometer high bumps on the polymer surface having a separation from a fraction to several micrometers.

4) A fourth excimer laser based polymer surface structure modification technique relies on producing small inert opaque particles on the surface of the film. These particles absorb or scatter the laser radiation but do not themselves decompose or ablate. Consequently they shadow the polymer material below them and give rise to the formation of cone like structures in the polymer as the laser radiation etches the

polymer on successive shots. Inert particles such as alumina or graphite may be introduced onto the surface or into the bulk of the material to give a wide variety of cone type structures [3]. The density and size of particles introduced defines the cone structure and separation scalelength.

Alternatively, particles can be introduced on the surface of the film by adjusting the laser irradiation conditions to work close to the threshold for UV laser photoablation. At such low fluences, material ablated is only partially decomposed and is ejected at low velocity so that microparticles and debris become redeposited onto the film surface and act to shadow it during subsequent pulses. The scale size of the cone like structures produced depends on the material, wavelength and laser fluence but separation scales of a few micrometers are readily achievable. The depth of the structure produced by the microparticle introduction method is determined by the number of laser pulses and fluence applied to the surface. Since the steep wall angle of the cone reduces the local fluence below the threshold required for etching, once a cone structure has started to form it tends to become stable, even if the opaque particle that seeded it is removed. Consequently, by the action of a large number of successive laser pulses structures as deep as many hundreds of micrometers can be produced.

Some aspects of the microstucturing techniques described above have been noted previously [3,4]. The *new inventions* described here are:

(i) the use of excimer laser radiation to chemically clean polymer films contaminated by hydrocarbon impurities and produce clean and chemically active surfaces.

(ii) the use of excimer laser radiation to produce free charges on the surface of polymer films.

(iii) the use of coherent excimer laser radiation and optical devices such as single and double biprisms to produce microstructures on polymer surfaces by crossing multiple grating patterns.

The fine scale surface structures and surface activation and charging and contamination removal and cleaning effects produced on polymer surfaces by the excimer laser methods described above can be used for a variety of new applications. Some of these applications rely on the roughened surface produced by the laser radiation. Others utilize the free charges produced on the surface or the chemically active nature of the surface following excimer laser irradiation.

A variety of these novel *applications* are described below:

(a) One major application is in the area of bonding of polymers to other polymers or other materials by the use of adhesives. Many polymers are notoriously difficult to bond by adhesives and frequently polymers must have their surface cleaned and

activated by chemical or plasma treatments in order to produce an adequate key for the adhesive. Excimer laser irradiation of the polymer surface by any of the methods described above can both roughen the surface to produce a greater surface area and better adhesive key and also clean and chemically activate the surface to provide greater polymer to adhesive bonding.
Typical examples of polymer materials that can be bonded more effectively after surface irradiation by excimer lasers are polyesters (polyethylene terphalate) and polyvinylidene fluoride. A very wide variety of other polymers can be treated in this way.

(b) Another application for excimer laser induced surface roughening of polymers is in those areas where it is necessary to increase surface friction to improve handling of film. Such a process can be termed laser microknurling as it can give similar results to conventional mechanical metal knurling that is used to increase friction and improve grip. As an example of the use of this process a laser roughened or knurled strip down each edge of a polymer film will improve winding stability and control. In other situations laser roughened regions on films can be used to enable rollers to grip more effectively and give better film control. Polyesters can be roughened very effectively by excimer laser irradiation although a large number of other polymers can be similarly treated by this technique.

(c) Another area of application of excimer laser roughened polymers utilizes the fact that the structures produced have scale sizes of a few micrometers and so very effectively scatter visible light. Since the roughened surface can be readily seen by eye or detected by optical sensors many new applications are possible. Polymer films and plastic objects can be readily laser marked with codes or trademarks for identification purposes. In other cases marks on polymer films produced by UV laser irradiation can be detected by photosensors to determine speed of the film, film breakage etc.
Identifiable marks can be imprinted on polymers using a few or in some cases only one laser pulse in conjunction with optical projection or contact masking techniques. Using coherent laser radiation and interference techniques, detectable grating structures can be placed on polymer surfaces with a single laser pulse by exposing the films or objects 'on the fly' when they are moving at speeds of up to several meters per second.

(d) The irregular surface structure produced on polymer films by any of the methods described above makes an ideal filter medium for separating particles which have sizes from a few micrometers down to a fraction of a micrometer from various fluids. By constraining the particle bearing fluid to pass over the roughened surface, particles with dimensions greater than the minimum structure size will be removed. A suitable filter device could consist of a laminated stack of polymer films with excimer laser roughened surface areas, each with arrays of holes to permit passage

of the fluid through from the foil above to the foil below such that each hole array is off set from the one above. Such a filter stack can be used to separate out such items as red blood cells from blood plasma or bacteria from other fluids. The filter system described above relies on the irregular surface structure to stop particles by obstructing their passage through the small apertures between the irregularities. As well as this surface structure excimer laser irradiation of the polymer gives rise to copious free surface charges which can selectively attract and bond to certain particles and molecules. By passing a variety of fluids over the surface of such charged areas of polymer, separation, filtration and trapping of selected contained molecules and particles that have nonsymmetic charge distributions can be achieved.

(e) Another important application of excimer laser surface modified polymer films relates to the manner in which polymer surfaces are wetted by various fluids. In general most synthetic polymers are hydrophobic and are poorly wetted by fluids such as water and alcohol. Excimer laser radiation of the surface of the polymer produces surface charges which cause a much higher degree of adhesion between the polymer and the fluid. In effect the surface becomes significantly more hydrophillic. Such an effect is useful in applications where fluids are in contact with or required to pass through polymer films such as filters, jets and hole arrays.
In addition such an effect can be used to render defined areas of printing plates hydrophyllic for lithography purposes. By UV laser irradiating areas in the form of characters or other defined shapes onto printing plates with appropriate plastic coating the exposed areas will be made to attract ink whereas the surrounding areas will remain hydrophobic.

(f) The deep cone like structures produced by irradiating polymers containing inert particles or at fluences near the threshold for laser ablation where partially decomposed material redeposits onto the surface find application in all of the areas described above. In addition such surfaces either by themselves or particularly when coated with thin metallic layers can be used as highly effective light absorbers or light traps. Incident visible and infrared radiation passes into the cone type structure and is reflected and absorbed at the sides of the cones down into the base of the material without reflection. Such a structure will have applications in areas where polymer films need to be made light absorbing to create a 'moth's eye' affect from which little incident visible or infrared radiation is reflected. A particular application of this type of material is as a covering for civil or military vehicles, aircraft or missiles such that if illuminated by any laser or other device emitting visible or infrared radiation such as a range finding system, bomb aiming device, or night vision system, no reflected signal is reradiated thus rendering the vehicle unobservable and undetectable to the device.

(g) Ancther application of polymer material which has been structured by UV laser

radiation to produce a deep high density cone type structure is as an acoustic absorber or damping material for hypersound waves having short wavelengths of comparable magnitude to the cone separation and depth scale size.

(h) Various of the roughened surfaces produced by UV laser radiation described above can be used as the basis for large area field emission cold cathode devices for high voltage electron beam systems. In this case the substrate on which the roughened surface is fabricated needs to be electrically conducting. Such a device can be fabricated by applying a thin layer of polymer to a metallic substrate and subsequently irradiating with UV laser radiation under appropriate conditions to produce a surface covered in a high density of cones. Laser etching through to the metallic backing followed by subsequent metalization of the roughened surface produces a suitable structure for operation as a field emitting cathode.

(i) The large surface areas provided by the cone type structures and microroughened surfaces produced on polymer surfaces by UV laser radiation can be used as an effective substrate for catalysts for chemical reactions. When coated with appropriate catalytic elements or compounds such structured polymer films can be fabricated into laminated structures similar to the fluid filter device described above to make devices for the promotion of catalytic conversion reactions.

References

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[2] Excimer laser beam homogeniser system. UK Patent Application No 8816423.1. 9th July 1988.
[3] Development and origin of conical structures on XeCl laser ablated polyimide. P E Dyer, S Jenkins, J Sidhu. Appl Phys Letts 49, 453 (1986).
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CLAIMS

PATENT APPLICATION NO. 8915000

1) The use of pulsed radiation in the ultra violet region of the spectrum generated by high power excimer lasers for the irradiation of the surface of polymers and other materials in order to remove hydrocarbon contaminants and produce a clean and chemically active surface.

2) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the generation of free electrical charges on the surface of the polymer film.

3) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the generation of micro roughened surfaces on various polymers for the purpose of improving the bonding strength of adhesives to the polymer.

4) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the purpose of increasing the frictional properties of the polymer surface.

5) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the purpose of reducing the reflected or back scattered optical and infrared radiation from the polymer surface.

6) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the purpose of making particle filtering devices.

7) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the purpose of marking the surface of the polymer film for identification purposes.

8) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the purpose of making large area field emission cold cathodes for high voltage electron beam generators.

9) The use of ultra violet radiation from pulsed excimer lasers as in **Claim 1** for the purpose of making large area surfaces for catalyst substrates.

10) The use of pulsed ultra violet radiation from excimer lasers as in **Claim 1** for the conversion of hydrophobic polymer surfaces into hydrophilic ones.

11) The use of coherent pulsed ultra violet radiation from high power excimer lasers with optical devices such as single, double and multiple biprisms to generate multiple crossed grating structures on the surface of polymer films in order to micro roughen the surface for any of the applications listed in **Claims 3 to 9** above.

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